

# EVALUATION OF ALUMINA QUALITY PARAMETERS

O.M. Bakkerud, J.A. Larsen\*  
B. Lillebuen\*\*

\*Hydro Aluminium, Oslo, Norway  
\*\*Hydro Research, Porsgrunn, Norway

## ABSTRACT

The physical and chemical properties of alumina from many refineries around the world are used in a discussion of the main quality parameters for the four Hydro Aluminium smelters in Norway.

The present evaluation and testing process preceding introduction of all new alumina qualities are described, and a review is given of the remaining issues that call for more research and investigations regarding the impact of alumina on smelter performance.

# EVALUATION OF ALUMINA QUALITY PARAMETERS

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## 1.0 INTRODUCTION

Initially, this paper gives a discussion of some important issues regarding alumina quality, and their impact on smelter performance.

The vital alumina quality parameters for Hydro Aluminium's smelters in Norway are presented, and typical data for 9 accepted alumina qualities, and 3 qualities under evaluation, are given.

The paper also describes Hydro Aluminium's evaluation procedure for testing and eventually accepting a new alumina.

Finally, the chemical and physical properties needed to meet Hydro Aluminium's alumina specification in 3-5 years are indicated.

## 2.0 ISSUES REGARDING ALUMINA QUALITY AND ITS IMPACT ON SMELTER PERFORMANCE

We will limit the discussion in this chapter to dust formation, dissolution, current efficiency, and sodium content in alumina.

### 2.1 Dust

#### 2.1.1 General

In addition to creating unwanted emissions and an unpleasant working environment in the smelter, dust will also give operational difficulties in air conveyor systems, in point feeders, during silo filling and discharge, and in the dry scrubbers.

Various attempts to make universal correlations between dusting and alumina parameters have given rather unclear conclusions (1).

#### 2.1.2 Dust tests

Fig. 1 shows the set-up for measurement of the Ravn dust index (2). The design of dust tests and the interpretation of the results from such tests, has a high degree of uncertainty. We believe nevertheless that the simplicity of the Ravn test is a plus, and it certainly measures the tendency of the alumina particle to be carried away by air (or other gases), which is a general mechanism for the creation of dusty environments.

FIGURE 1: APPARATUS FOR MEASUREMENT OF RAVN DUST INDEX

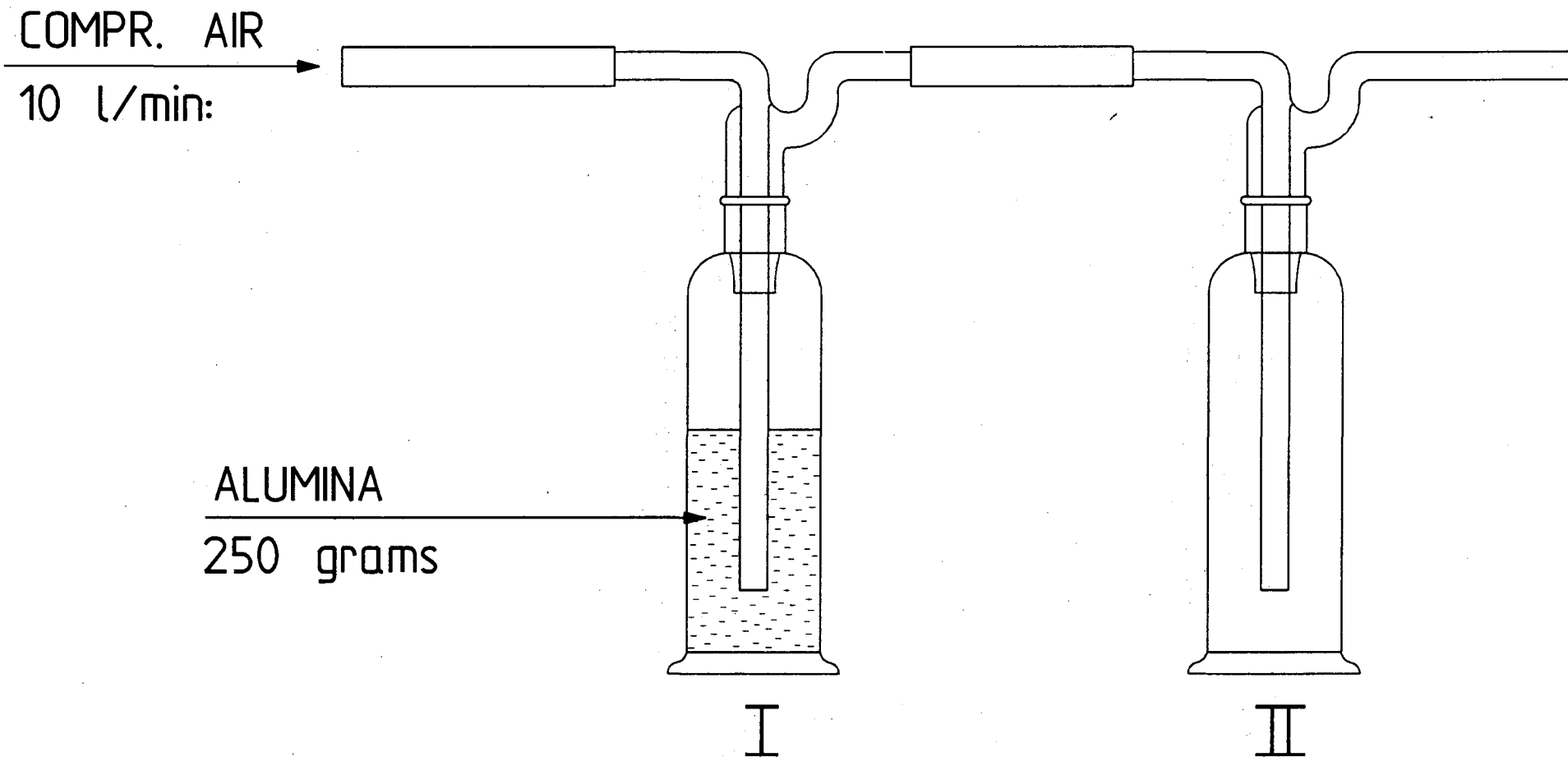


Fig. 2 shows measurements on composite samples from 35 shipments of alumina over a period of 10 years, from two different refineries.

As Fig. 2 shows, there is a correlation between LOI and dust index, so that higher LOI gives higher dust index, more or less as expected.

The thing to note is the splitting up of the data into two groups. The upper, small group of 8 shipments are results on shipments from one of the refineries when it produced an alumina with high amounts of fines and low LOI ("semi-sandy"). The lower line are data points from the refineries when they both made sandy alumina.

Fig. 3 shows dust index plotted versus fines fraction (-45 mm).

Finally we made a regression equation of the form

$$\text{Dust Index} = a_0 + a_1 \cdot [\text{fines}] + a_2 \cdot [\text{fines}]^2 + a_3 \cdot [\text{LOI}] \cdot [\text{fines}]$$

from all the data, and Fig. 4 is a display of this equation. As expected, the effect of fines is much larger than the effect of LOI, for this type of simulated dusting behaviour. In particular at low fines content, there is a steep increase in dust index for a small increase in fines.

The measurements discussed here were done some years ago, and superfines (-20  $\mu\text{m}$ ) were not analysed.

### 2.1.3 "Geyser" dusting

Another dusting process associated with alumina of high LOI, is the so-called geyser effect, caused by sudden evolution of water vapour when alumina hits the hot bath, thus carrying fines into the potroom air or into the cell gas.

This effect is not simulated by any of the existing dust tests (3), but from our practical experience, we should limit  $\text{LOI}_{300 \rightarrow 1000}$  to a maximum of about 1.0 - 1.2% for this reason. This will be further discussed in the paragraph on alumina dissolution.

### 2.1.4 Segregation and uneven product quality

In smelters, dust may very much be a problem because of uneven alumina quality, both w.r.t. fines content and w.r.t. degree of calcination.

Since one of the main technological challenges in Bayer plants is to increase yield in precipitation, keeping control of particle size is for many refineries a constant problem. Impure bauxites, with substantial amounts of organic impurities, and the lack of reliable liquor purification processes, in combination with the need to limit caustic

FIGURE 2: DUST INDEX VERSUS LOI

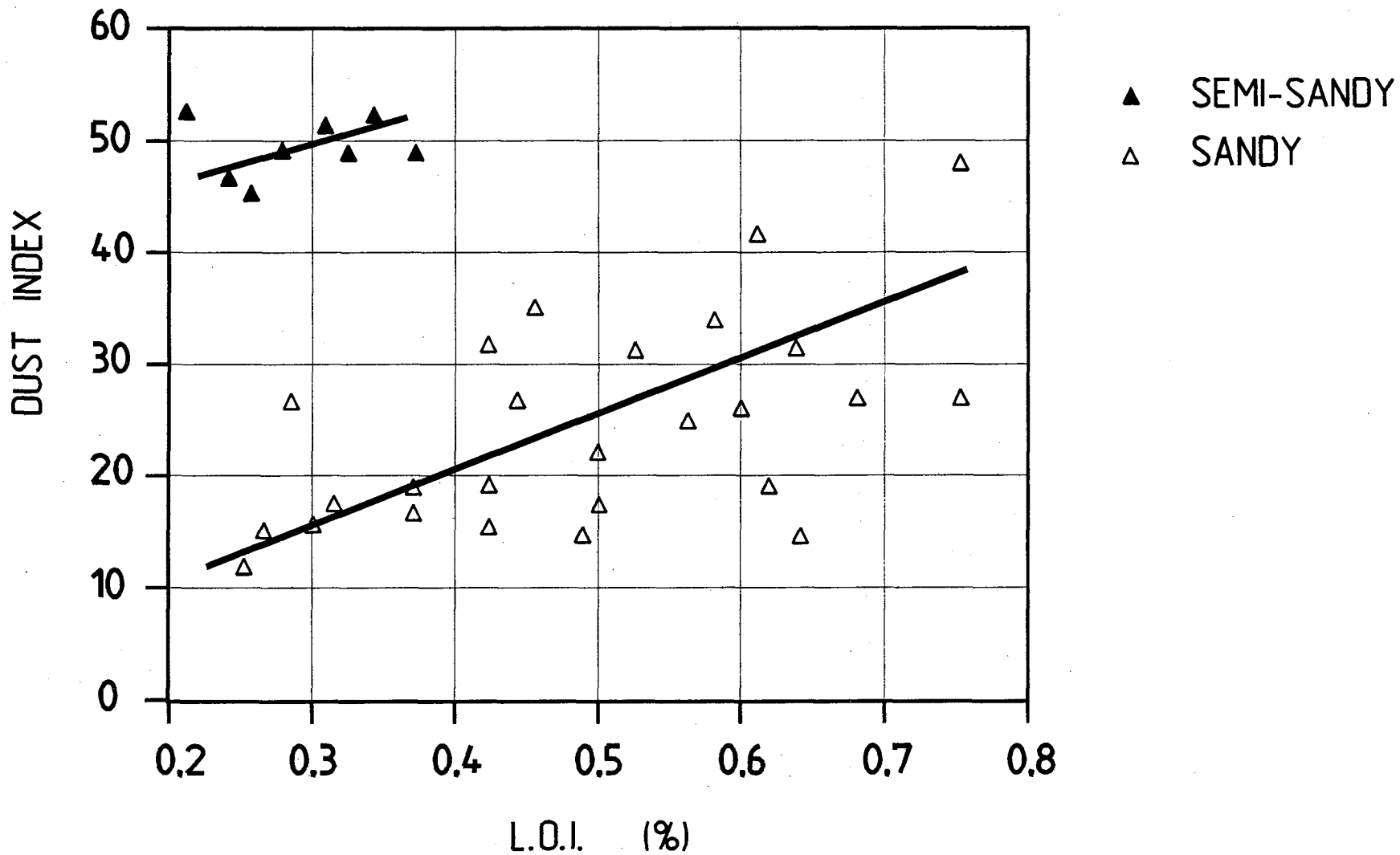


FIGURE 3: DUST INDEX VERSUS FINES FRACTION

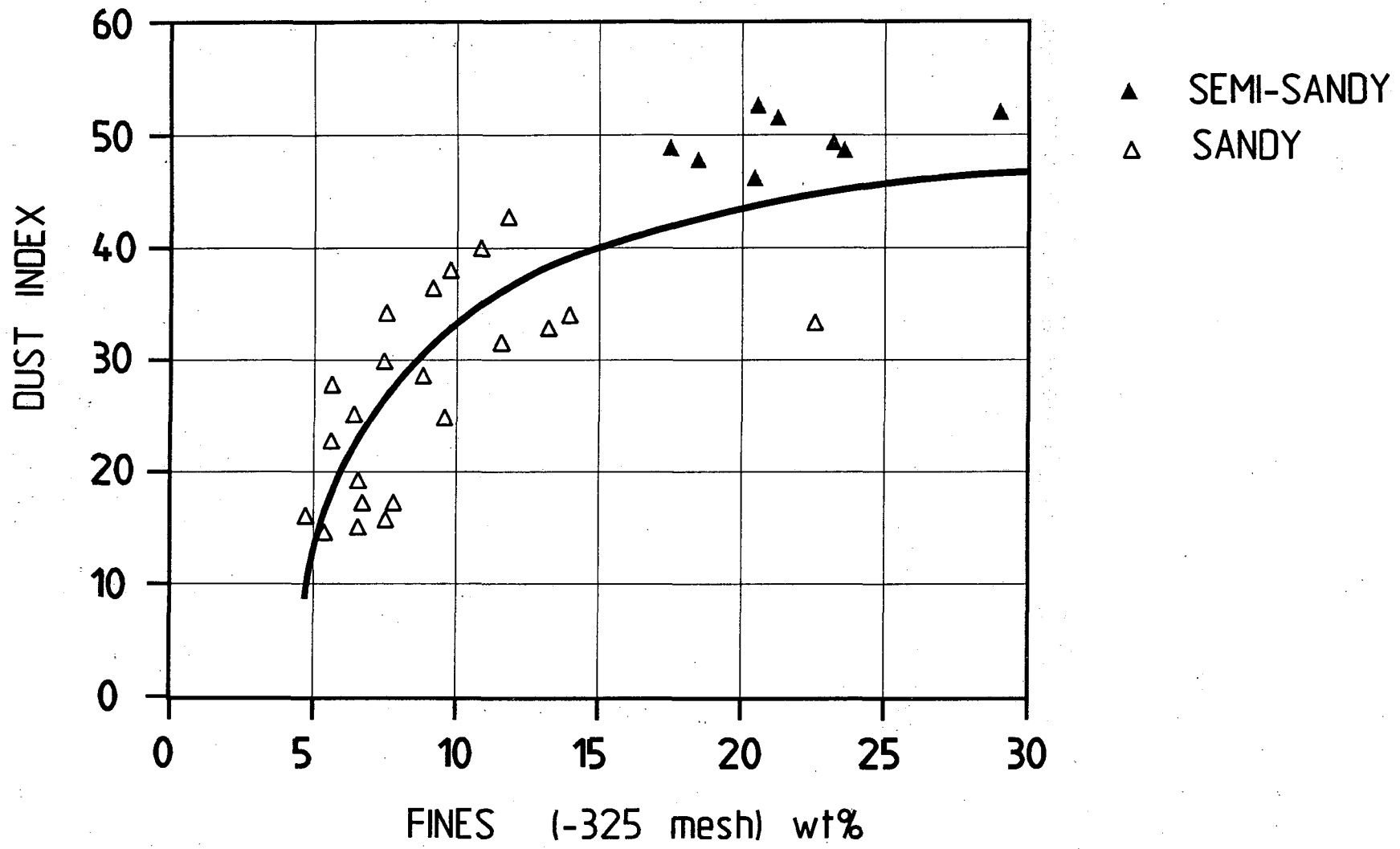
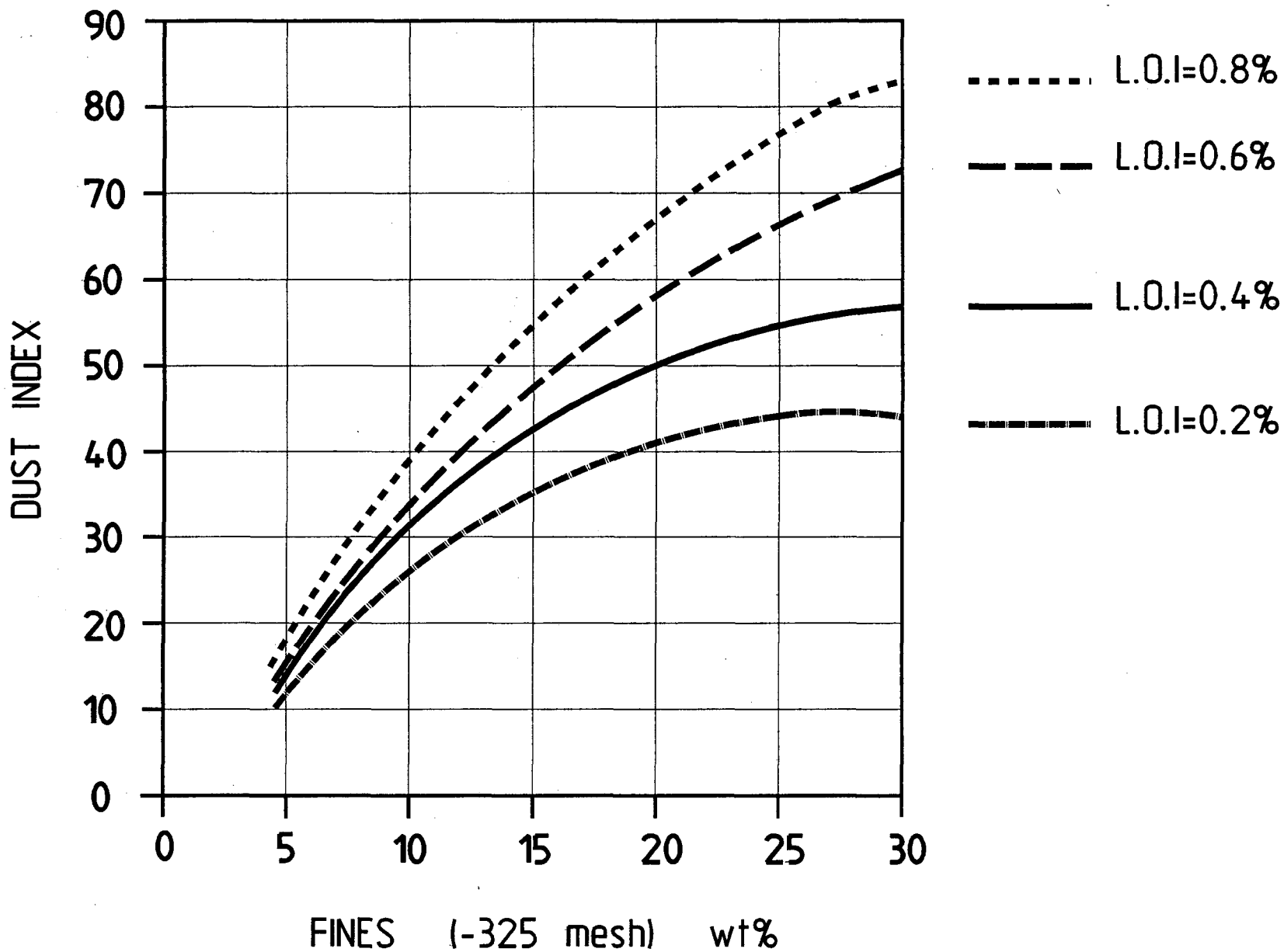


FIGURE 4: DUST INDEX VERSUS FINES AT CONSTANT LOI



emissions, are causing frequent deviations in the precipitation circuits, and leading to the production of too much fines in some periods.

Also, many stationary calciners generate more fines than desired, because the precipitation circuit does not produce hydrate particles with sufficient strength, or the calciner is very abrasive.

Most existing alumina silos do have segregation problems. Although we know quite a few things about how to design and operate them to minimize segregation, this still remains a major cause of periodical dust problems in many smelters.

### 2.1.5 Superfines

A particular concern is the superfines, i.e.  $-20\ \mu\text{m}$  fraction.

As demonstrated by many laboratories, the amount of superfines is critical for the free flowing of alumina, which again is very important for the operation of dry scrubbers, air conveyors, and point feeders. As is to be discussed later, it is also of primary importance for the dissolution behaviour of alumina, and it has been shown by Bertaud et al. (4) that the dust samples collected in various parts of the potroom have a dominant fraction of fines and, above all, of superfines.

The ESP-dust which may be a major part of the superfines, is one of the remaining problems in the Bayer plants. From a "dusting" point of view, it should at least be returned to the kiln for more calcination instead of being added directly to the product. Even better, from almost every point of view, would be to do away with ESP-dust altogether, and some possibilities exist: The use of ESP-dust as seed has been suggested, redigestion should be possible, and the dust may be refined into special type alumina products. (5)

Today, however, almost every refinery leaves the problem for the smelter to deal with, which is highly unsatisfactory in the opinion of most smelter operators (6).

It is very likely that future alumina purchase contracts will contain specifications for the  $-20\ \mu\text{m}$  content. It will then be necessary to describe in detail the applied analytical procedure.

## 2.2 Dissolution

### 2.2.1 General

If alumina is dissolved in molten cryolitic baths grain by grain, the dissolution time is very short (10 - 20 seconds).



Dissolution in commercial cells is, however, very much a question of heat transport: One dose from a point-feeder is dissolved in about one minute, and one "break" in the traditional side - or center-break cells may need hours to dissolve.

When discussing alumina quality from a dissolution point of view, it is therefore not the solubility as such, but more the crust-forming ability which counts. Dissolution is, at the beginning, a slow melt-down of the frozen clumps of cryolite and alumina that form when cold alumina contacts the molten bath, followed by a fast dissolution and distribution in the bath.

### 2.2.2 Crust formation

Taking crust to be any mix of frozen bath and alumina aggregates, we know from previous investigations (7,8):

- Given time (hours) to recrystallize and grow, the  $\alpha$ -alumina crystals in the crust structure will need very long time to dissolve.
- Low  $\alpha$ -alumina will form a stronger crust than high  $\alpha$ -alumina due to the reinforcement by the  $\gamma \rightarrow \alpha$  crystal transformation and building.
- High-LOI alumina, and alumina that has been through a dry scrubber, will disperse to a larger extent when entering the bath from a point-feeder than virgin alumina and alumina with a low LOI. This is very significant for the crust formation, and for the subsequent melting and dissolution.
- Fines and superfines will disturb the flow of alumina and thereby also disturb the crust formation and subsequent dissolution.
- Too much of coarse and fine particles (inhomogeneous material) disturb the wetting of alumina particles with molten bath, and may therefore also influence crust properties.
- Very high LOI sometimes generate a problem for point-feeders because the geysers expel fine alumina particles, building up around the feed hole or escaping into the pot gases.

### 2.2.3 Side - or centre break cells

Most of the 100 - 200 kg of crust and alumina added by traditional side- or center-breaking, will inevitably fall down on the side-ledge or on the cell bottom beneath the metal, to be dissolved from there.

The dissolution process is very slow (hours), and availability of heat and stirring seems to be limiting factors, along with metal- and bath height and the shape of the side-freeze.

Also, if low-LOI alumina forms a crust sufficiently strong for sealing in a side- or centre-break cell type, it may be easier to dissolve this crust than the crust from a high-LOI alumina, due to the effect of  $\alpha$ -crystallization and growth mentioned above.

In modern smelters though, dry scrubbing is necessary, requiring sandy alumina with relatively low  $\alpha$  and high LOI.

Formation of the crust seal sometimes creates a problem. We have experienced a few cases of extremely strong crust with low  $\alpha$ -alumina, so strong in fact that it has resulted in operational problems, because the breaker has been unable to punch holes in the crust.

Other alumina qualities with similar low content of  $\alpha$ -alumina (0-3 wt%), did not, however, give abnormally strong crust. We have investigated this phenomena, looking for explanations from the content of intermediate alumina-phases, i.e. those between  $\alpha$  and  $\gamma$ , looking for hydrate (gibbsite) content, and particle size distribution, etc., but so far being unable to come up with satisfactory correlations, thus leaving the area open for more research.

#### 2.2.4 Point-feeding cells

Turning to the case of point-feeders for alumina, every point-feeder design will probably have an optimum alumina quality.

The point-feeders may differ in

- size of doses (1 - 5 kg)
- dose frequency (10 - 300 sec.)
- feeder design
- breaker design and operation

All of these factors will influence the optimum alumina quality requirement to some extent.

In general, experience on plant cells, as well as from laboratory experiments, indicates that high-LOI alumina dissolves faster than low-LOI alumina when added as small doses.

The difference may be up to 50% when changing from 0.9% LOI to 0.5% LOI (9). This may not, however, be significant, as long as the time between doses remains sufficient for one dose to dissolve completely before the next is added (10).

There seems to be an upper limit, around 1.0 - 1.2% LOI, above which some point-feeder cells experience problems. This has been explained as build-up of  $\alpha$ -alumina around the feeder holes, deposited there after having been blown out of the melt by the geysier-effect.

Others seem to believe that such high LOI leads to expelling of fines, which are carried away with the pot-gas, making the process- and feed-control difficult to manage.

None of these explanations are entirely convincing, leaving the area open for research and improvements.

Returning to the role of fines, their influence on dissolution may arise as a consequence of their varying degree of calcination (as is often the case for ESP-dust) when compared with the average alumina particle. If the fines accumulate, due to silo segregation, they will then cause variable dissolution behaviour in the cells.

The fines and superfines also have a distinct influence on the flow properties of the alumina, making it flow less freely.

This again may have a very significant effect on the crust formation process, and therefore also on the subsequent remelting and dissolution in point-feeding cells.

Again, this is an area open for, and in need of, more fundamental and applied insight.

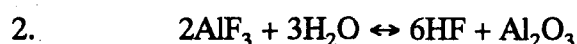
## 2.3 Sodium Oxide

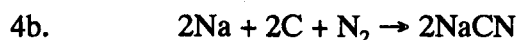
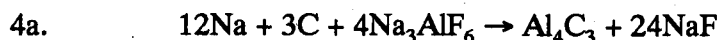
The sodium in alumina plays an important role in the bath chemistry and in the feed and process control of the cell.

Keeping the excess  $\text{AlF}_3$ -content within narrow limits is an important task in all pot-lines with  $\text{AlF}_3$ - $\text{CaF}_2$ -cryolite bath, since the excess  $\text{AlF}_3$ -content influences bath temperature, current efficiency, alumina solubility etc. This is not easy, since it involves at least four more or less independent reactions that contribute or consume  $\text{NaF}$ ,  $\text{Na}_3\text{AlF}_6$  or  $\text{AlF}_3$ :



The other reactions are, if the small emission losses are neglected:





In addition to reaction 1, which is the direct effect of sodium on the  $\text{AlF}_3$ -balance, this balance is also influenced by return of adsorbed HF picked up by alumina in the dry scrubbers (reaction 2); by disturbances in the thermal balance of the cell (freezing and melting of cryolite, reaction 3); and finally by the impregnation of the cathode carbon (reactions 4a - 4c).

In the context of a complete smelter over a longer period of time, reaction 1 and reactions 4a - 4c should be in equilibrium, so that reaction 4 consumes the same amount of cryolite as reaction 1 is producing.

With longer cathode life times, and probably some degree of recovery of the fluoride in the spent pot lining, it seems realistic to expect that smelters will demand  $\text{Na}_2\text{O}$ -contents well below 0.4% in the future. This will be a challenge for most of the Bayer plants. It is not difficult to make low sodium alumina, but it is difficult to make low sodium alumina without loosing on liquor productivity and energy consumption in the Bayer plant.

Further fundamental research into the precipitation process is therefore needed to bring about the cost-effective production of low-sodium alumina.

Reaction 3, the thermal balance of the cell, is not directly connected with the alumina quality. Reaction 2, fluorine recovery in the dry scrubber, illustrates the general need for a more even and stable quality of alumina. The operation of the dry scrubber will vary with the fines content and the surface area of the alumina, and so will the fluoride content of the alumina taken to the cells.

This variation makes life more difficult for the cell computer and the cell operators, since it will influence and change bath temperature, current efficiency and metal production, as well as plant emissions.

Many of the large prebake cells with point-feeders, experience problems when the operators try to run them above 12 wt% excess  $\text{AlF}_3$ . This may have a number of reasons, one of which could be the alumina dissolution rate. We have made investigations which indicate that rather the distribution of alumina-rich bath may be one of the limiting factors. Obviously, more work is needed for clarification.

## 2.4 Current Efficiency and Impurities

Recent laboratory work (11) seems to support early theories that some impurities, in particular phosphorous, but also Fe, V, Zn, Si, Ga and Ti can have a detrimental effect on current efficiency. This could, if verified, put more

pressure on the refineries, since alumina is one of the major supplier of such impurities to the electrolytic cells.

### 3.0 ALUMINA QUALITY PARAMETERS IN HYDRO ALUMINIUM

Presently, 9 different aluminas have been accepted in the four Hydro Aluminium smelters in Norway, and 3 aluminas are under evaluation. Typical chemical and physical data for these 12 products are given in appendix 1.

#### 3.1 Important Quality Parameters

##### 3.1.1 Introduction

The physical specifications will have an impact on handling and storage, dry scrubbing, electrolysis and emissions. The chemical specifications will influence pot operation and metal purity.

##### 3.1.2 Physical properties

The physical parameters considered the most important by Hydro Aluminium are listed in Table 3.1:

Table 3.1 - Important physical parameters in alumina

Parameter	Affecting		Typical values <sup>1)</sup>			
			Ave.	Max.	Min.	
Granulometry <sup>2)</sup>	Segregation	+100 Mesh	%	3.1	8.0	0.0
	Flowability	-325 Mesh	%	8.3	11.0	6.0
	Dustiness	-20 µm	%	1.45	3.0	1.0
	Dissolution					
Loss on Ignition	Flowability	LOI(300-1000°C)	%	0.77	0.95	0.60
	Dissolution					
	F-recovery					
	Dustiness					
	Crusting					
Surface Area	Flowability	BET	m <sup>2</sup> /g	68.8	85	60
	Dissolution					
	F-recovery					
	Crusting					

1) Based on the 12 aluminas listed in appendix 1.

2) Based on analysis from dry sieving. -20 µm data are mostly based on various laser methods.

Granulometry is a property that is getting a lot of attention, especially the superfines (-20 µm), due to optimization of the operations in

general, and stricter environmental regulations facing the smelters. Also attrition index is an important factor in this context, at least for smelters with modern dense phase transportation systems.

LOI and BET are directly correlated (higher BET gives higher LOI), but the correlation factor will depend on the calcination process. Modern dry scrubbing processing today seems to be very efficient even with BET in the 60-65 m<sup>2</sup>/g range. In the Hydro Aluminium smelters, there is a tendency to prefer a lower LOI, but not lower than resulting in satisfying results environmentally, today and in the future.

### 3.1.3 Chemical properties

A list of the most important chemical parameters in alumina, as evaluated by Hydro Aluminium's smelters, is given in Table 3.2.

Table 3.2 - Important chemical parameters in alumina

Parameter	Affecting	Typical values <sup>1)</sup>		
		Average %	Max. %	Min. %
Na <sub>2</sub> O	Bath composition Amount of bath Process control	0.43	0.52	0.35
CaO	Bath composition	0.030	0.053	0.003
Fe <sub>2</sub> O <sub>3</sub>	Metal purity	0.013	0.020	0.005
SiO <sub>2</sub>	Metal purity	0.013	0.020	0.010
P <sub>2</sub> O <sub>5</sub>	Metal purity Current efficiency	0.0010	0.0018	<0.001

1) Based on the 12 aluminas listed in appendix 1.

For sodium, a total balance around a cell will decide the equilibrium amount of Na<sub>2</sub>O required from the alumina. Big variations in Na<sub>2</sub>O content from shipment to shipment will cause disturbances in the operation.

CaF<sub>2</sub> in the bath is important because of temperature and density control. Low CaO content in the alumina can be compensated by adding CaF<sub>2</sub> to the cells.

The market seems to require higher and higher purity of the metal. Most focus is put on Fe<sub>2</sub>O<sub>3</sub>, but also SiO<sub>2</sub> is an important parameter in this context. Metal purity is a concern when using aluminas with a

considerable amount of ZnO, which is the case for Jamaican and Greek aluminas.

Phosphorous in the bath has proved to have a negative effect on current efficiency. However, there is a need to get more full scale data in terms of, among other things, how much the alumina is contributing to the final phosphorous content in the bath. This problem is also relevant for vanadium.

#### **4.0 EVALUATION AND TESTING PROCEDURE OF AN ALUMINA IN HYDRO ALUMINIUM**

In appendix 2 is a schematic flowsheet, showing the necessary steps to be taken before an alumina is approved in a Hydro Aluminium smelter.

The individual steps in the flowsheet should be more or less self-explanatory.

The evaluation period goes on from the ship starts unloading at the port, continues during the physical test period, till a final report is submitted. The final report will normally discuss the following:

- Certificates of analysis.
- Unloading, handling and internal transportation.
- Dry scrubbing experience.
- Electrolysis (bath composition and temperature, crust formation, dissolution, sludge formation, disturbances, anode effects, energy consumption, consumption of  $AlF_3$  etc.).
- Metal purity.
- Environment (dust emissions over roof, working atmosphere, F-emissions, other).

The report is frequently edited as a "deviation report", meaning that nothing is reported on the various subjects above if the evaluated alumina does not differ from the alumina quality giving normal smelting conditions.

At the end of the report, the smelter concludes whether the alumina is accepted, if another shipment is needed before it eventually can be accepted, or if the alumina is not accepted at the specific smelter.

In the future Hydro Aluminium will make quality audits, based on the ISO 9002 standard, of all its biggest suppliers of alumina. Alumina producers following an internationally recognized quality program, will be treated as approved suppliers.

## 5.0 HYDRO ALUMINIUM'S FUTURE ALUMINA SPECIFICATION

Through continuous discussions over the past years, including comprehensive evaluation exercises among our smelters, Hydro Aluminum has concluded that the following alumina specification is realistic in 3-5 years (indicative numbers):

Table 5.1 - Future alumina specification

Parameter	Specification
Fe <sub>2</sub> O <sub>3</sub>	< 0.01%
SiO <sub>2</sub>	< 0.01%
Na <sub>2</sub> O	0.35 - 0.40%
CaO	0.035 - 0.045%
TiO <sub>2</sub>	< 0.003%
ZnO	< 0.008%
P <sub>2</sub> O <sub>5</sub>	< 0.001%
V <sub>2</sub> O <sub>5</sub>	< 0.002%
BET	60 - 80 m <sup>2</sup> /g
LOI (300-1000 °C)	0.6 - 0.8%
Loose density <sup>1)</sup>	0.92 - 0.98g/cm <sup>3</sup>
Attrition Index	< 15%
Granulometry	
+100 Mesh:	< 5%
-325 Mesh:	< 7%
-20 µm:	< 1%

1) The most important factor is to keep variations less than 2%.

The above figures should be based on representative samples for each 2000 tons of alumina.

Further research and investigations might change some of these numbers.

On the other hand, we know that some of the alumina plants around the world today have limitations, that probably will exclude them if the above specification is strictly applied.

## 6.0 CONCLUSION

The main challenges for the Bayer plants will be to do away with superfines, to lower the sodium content and several other impurities in the alumina, and to maintain a more even alumina quality, without losing on cost effectiveness, liquor productivity or plant emissions.

The smelters should improve their control of segregation and attrition of alumina, gain more insight into the dissolution and distribution of alumina in cells with point-feeders, and develop better computer and operator control of the bath chemistry.



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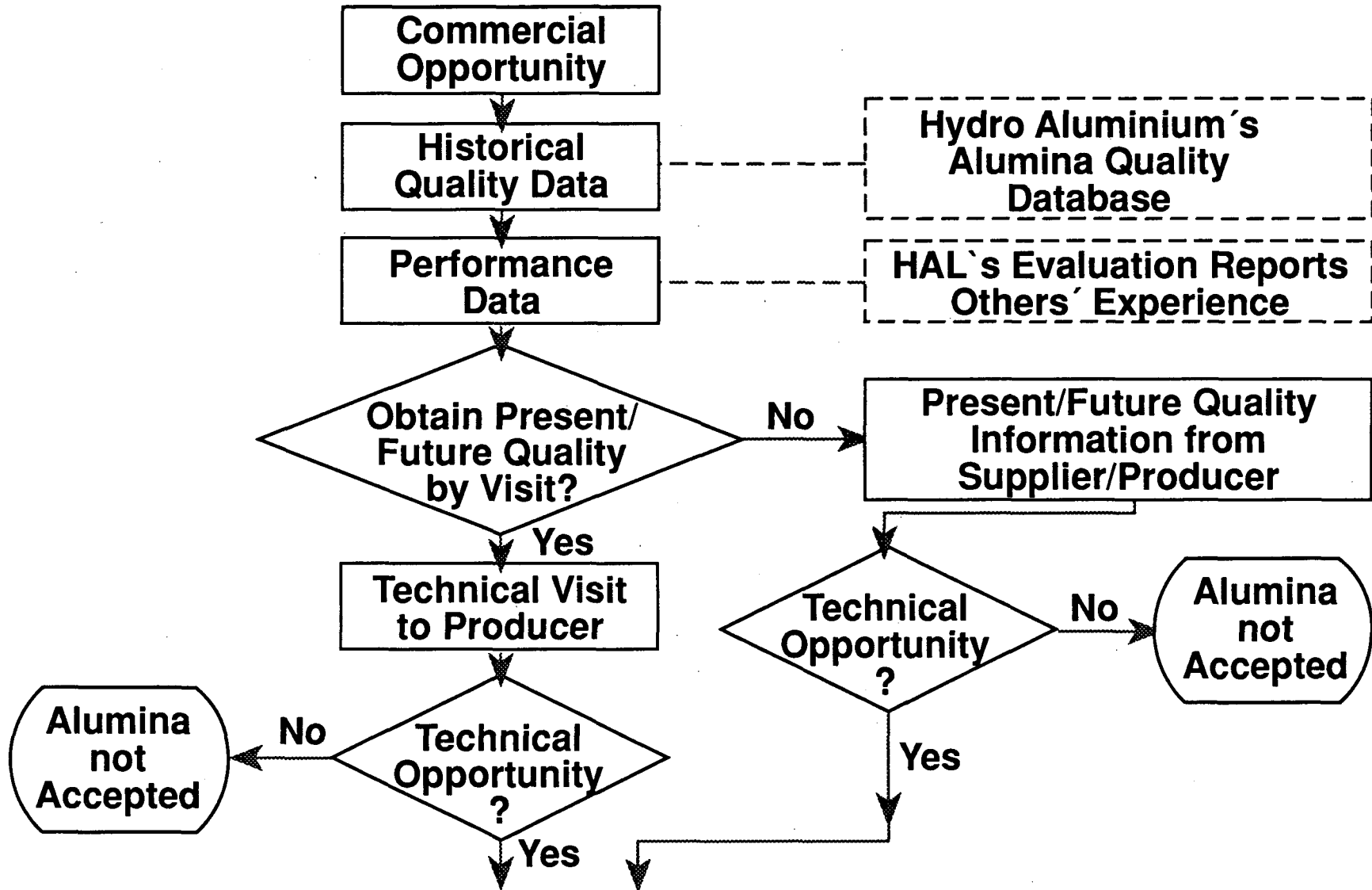
# TYPICAL SPECIFICATIONS FOR ALUMINAS IN HYDRO ALUMINIUM

Alumina no.	1	2	3	4	5	6	7	8	9	10	11	12	Aver	Max	Min
SiO <sub>2</sub> , %	0,013	0,015	0,010	0,010	0,010	0,015	0,010	0,014	0,014	0,013	0,015	0,020	0,013	0,020	0,010
Fe <sub>2</sub> O <sub>3</sub> , %	0,008	0,013	0,019	0,020	0,015	0,008	0,014	0,009	0,015	0,005	0,015	0,016	0,013	0,020	0,005
Na <sub>2</sub> O, %	0,52	0,43	0,35	0,40	0,38	0,45	0,40	0,44	0,48	0,44	0,42	0,40	0,426	0,520	0,350
CaO, %	0,053	0,041	0,007	0,003	0,025	0,040	0,045	0,020	0,045	0,030	0,045	0,007	0,030	0,053	0,003
P <sub>2</sub> O <sub>5</sub> , %	0	0,0018	0,0010	0,0010	0,0010	0,0005	0,0012	0,0010	0,0010	0,0010	0,0010		0,0010	0,0018	0,0000
V <sub>2</sub> O <sub>5</sub> , %	0,0010	0,0025	0,0010	0,0020	0,0020	0,0010	0,0010	0,0020	0,0010	0,0020	0,0012		0,0015	0,0025	0,0010
ZnO, %	0,0080	0,0005	0,0020	0,0010	0,0010	0,0100	0,0120	0,0010	0	0,0010	0,0005		0,0034	0,0120	0,0000
LOI, %	0,90	0,75	0,70	0,60	0,75	0,90	0,70	0,70	0,85	0,95	0,70	0,75	0,77	0,95	0,60
BET, m <sup>2</sup> /g	70	65	65	60	75	85	60	75	65	75	65	65	68,8	85,0	60,0
+100 Mesh, %	5	2	1	3	1	0	1	5	4	4		8	3,1	8,0	0,0
-325 Mesh, %	6	8	8	7	6	9	10	11	8	7	10	10	8,3	11,0	6,0
-20 μm, %	1	1	1,5	2	1	1	2	3	1,5	1	1		1,45	3,00	1,0



HYDRO  
ALUMINIUM

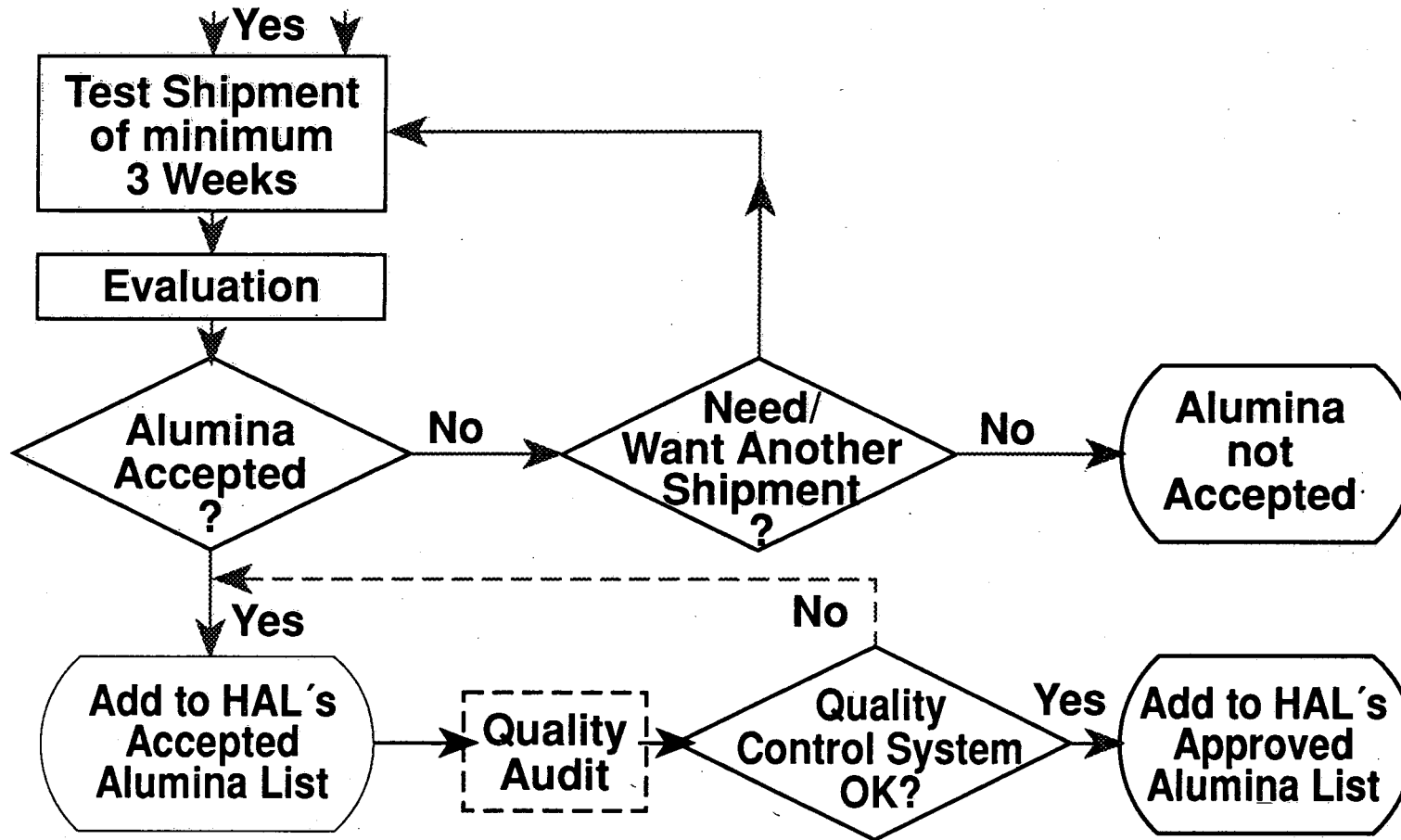
# ALUMINA QUALITY FLOWSHEET



EVALUATION OF ALUMINA QUALITY PARAMETERS

BAKKERUD, LARSEN & LILIBUEN  
PAGE 66

# ALUMINA QUALITY FLOWSHEET



EVALUATION OF ALUMINA QUALITY PARAMETERS

BAKKERUD, LARSEN & LILIBUEN  
PAGE 67